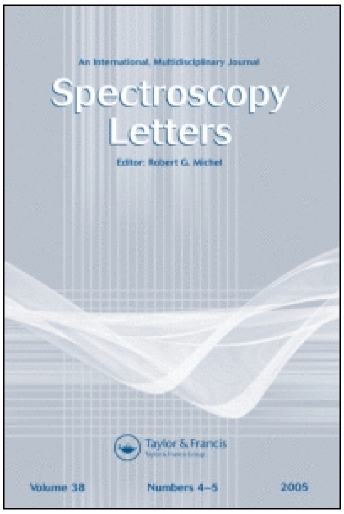

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Fourier Transform-Infrared Spectroscopic Study of Isonicotinamide Metal(II) Tetracyanonickelate and Halide Complexes

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Fourier Transform-Infrared Spectroscopic Study of Isonicotinamide Metal(II) Tetracyanonickelate and Halide Complexes

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ABSTRACT

In this study, fourier transform-infrared FT-IR spectra of $M(iso)_2Ni(CN)_4$ (where M = Cd, Zn, Ni, or Cu; iso = isonicotinamide; abbreviated to M–Ni-iso) and $Cd(iso)_2X_2$ (where X = Cl, Br, or I) complexes are reported in the 4000–400 cm^{-1} range. Vibrational assignments are given for all the observed bands. The analysis of the vibrational spectra indicates that there are some structure–spectra correlations. The proposed structure of tetracyanonickelate complexes consists of polymeric layers of $|M{-}Ni(CN)_4|_\infty$ with the isonicotinamide molecules bound directly to the metal (M).

Key Words: Hofmann-type complexes; Isonicotinamide; Infrared spectra; Tetracyanonickelate.

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1. INTRODUCTION

Isonicotinamide, a pyridine derivative with an amido group ($-CONH_2$) in the γ-position possesses strong anti-tubercular, anti-pyretic, fibrinolytic, and anti-bacterial properties. Because of their pharmacological effects mixed salts of isonicotinamide find extensive use as drugs in various biological and medicinal processes. Metal complexes of biologically important ligands are sometimes more effective than the free ligands.[1]

In our previous work[2] we reported the IR spectra of $M(iso)_2X_2$ (M = Co, Mn, Zn; X = Cl, Br) and $M(iso)_2X_2$ (M = Zn, Cu, X = I; M = Hg; X = Br) complexes. Here we continue with preparing four new iso metal(II) tetracyanonickelate $M(iso)_2Ni(CN)_4$ (M = Cd, Zn, Ni, or Cu) and cadmium halide complexes. The crystal structure of dipyridine-cadmium tetracyanonickelate complex was determined crystallographically in Ref.[3]. The tetracyanonickelate complexes are also analogous to the Hofmann-type complexes $[M(NH_3)_2Ni(CN)_4]$ and clathrates $[M(NH_3)_2Ni(CN)_4 \cdot 2G$; G = Guest molecule].[4,5] The structure of these complexes and the host lattice of the clathrates consists of two-dimensional polymeric layers formed from tetracyanonickelate ion bridged by coordinating diamine metal(II) cations and the layers lie one above the other.[4,5]

The aim of this study is to give further examples of layered tetracyanonickelate and cadmium halide complexes.

2. EXPERIMENTAL

2.1. Synthesis of Complexes

The isonicotinamide (Aldrich) was used without further purification. The potassium tetracyanonickelate was prepared by mixing stoichiometric amounts of nickel(II) chloride with potassium cyanide in water solution. All the other chemicals used were reagent grade (Merck).

$M(iso)_2Ni(CN)_4$ was prepared by dissolving 1 mmol of $K_2Ni(CN)_4$ in water. To this solution, 2 mmol of the ligand (isonicotinamide) and 1 mmol of the metal halide dissolved in ethanol was added, respectively. The reaction mixture was stirred for a few days at room temperature. The product obtained was filtered and washed with ethanol and dried in a vacuum desiccator.

$Cd(iso)_2X_2$ (X = Cl, Br, or I) was prepared by addition of the appropriate quantity of iso to a saturated solution of the metal halide in ethanol. The mixture was stirred magnetically at room temperature for two days. The precipated complexes were filtered, washed with ether, and dried.

2.2. Analyses and Measurements

The prepared samples were analyzed for C, H, and N with a LECO CHN-932 analyzer. The analytical data are reported in Table 1.

Infrared spectra (KBr discs or Nujol mulls) were recorded on a Mattson 1000 FTIR spectrometer, which was calibrated using polystyrene bands.

3. RESULTS AND DISCUSSION

3.1. Isonicotinamide Vibrations

The infrared spectrum of free isonicotinamide is given in Fig. 1. If we assume the amido group ($-CONH_2$) has a single mass point, all the molecules under consideration would belong to C_{2v} point group. This simplified model leads to 27 normal vibrations of which 19 are planar, and 8 are nonplanar. In addition to these 27-ring vibrations, there would be an additional 9 vibrations due to the substituent amido group. These vibrations cannot be classified as to their symmetry with respect to the molecular plane as the amido group makes the molecule nonplanar.

The vibrational wavenumbers of iso for the $M(iso)_2Ni(CN)_4$ (M = Cd, Zn, Ni, or Cu) complexes are listed in Table 2, together with the general assignments, taken from our previous work.[2] The vibrational assignments for a few bands of isonicotinamide were made by Yoshida,[6] and Ahuja and Prasad.[1] The vibrational wavenumbers and assignments of the free iso in Ref.[2] is in agreement with that of Ahuja and Prasad,[1] but Tocon et al.,[7] and Draeger[8] have reported some new theoretical calculations for pyridine and methyl pyridine results by using the scaled quantum mechanical force field (SQMFF) and normal coordinate analyses methodology, respectively. There are some differences for a few bands. For example the modes at 1496, 1410, 1063, 671, and 486 cm^{-1} are assigned i.p. CH (py), CC str (py) + i.p.

Table 1. Analytical data for compounds prepared.

	C (%)		H (%)		N (%)	
Compound	Found	Calculated	Found	Calculated	Found	Calculated
$Cd(iso)_2Ni(CN)_4$	31.71	31.00	1.81	1.51	20.82	21.18
$Zn(iso)_2Ni(CN)_4$	35.80	34.95	2.04	1.81	23.70	24.03
$Cd(iso)_2Cl_2$	33.56	33.67	2.64	2.80	12.80	13.09
$Ni(iso)_2Cl_2$	38.57	38.51	3.19	3.20	14.81	14.97

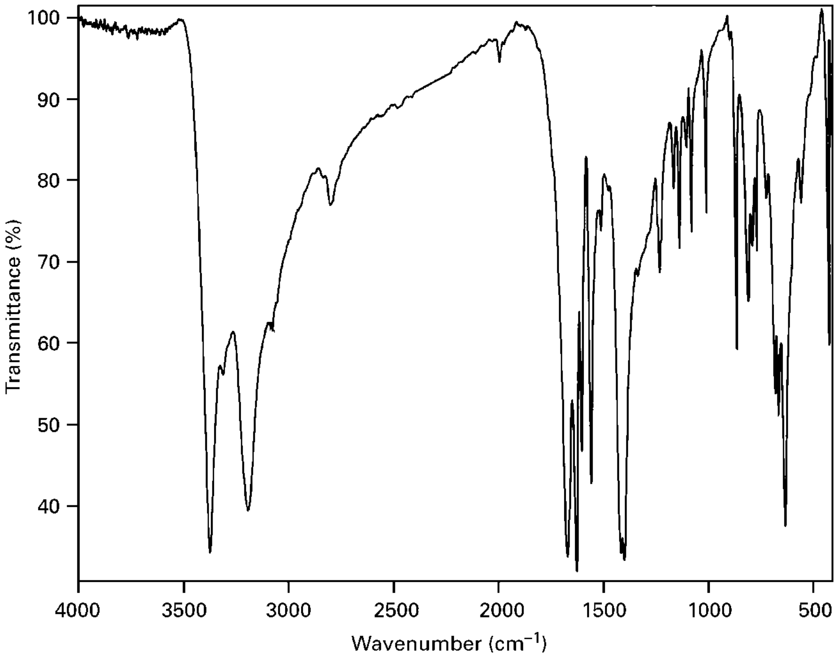

Figure 1. The infrared spectrum of isonicotinamide (in KBr).

CH (py), ring CCC bend, ring CCC bend, and ring torsion, respectively.[8] These are also given in Table 2. Isonicotinamide gives three donor sites: (a) pyridine ring nitrogen; (b) amino nitrogen; and (c) carbonyl oxygen. As a monodentate ligand the bonding may take place through either the pyridine ring nitrogen or the amino nitrogen or the carbonyl oxygen.

Significant absorption bands due to the amido group in isonicotinamide are ν(NH) (3370, 3187 cm^{-1}), ν(CO) (1668 cm^{-1}), and ν(CN) (1391 cm^{-1}). In complexes of amides [9] and other carbonyl donors [10] a significant negative shift of the carbonyl frequency takes place because of coordination through the carbonyl oxygen. The carbonyl frequency (1668 cm^{-1}) of the uncoordinated isonicotinamide does not undergo negative shift in the metal(II) halide tetracyanonickelate and cadmium halide isonicotinamide complexes studied here. Similarly, the ν(NH) and ν(CN) frequencies of the uncoordinated isonicotinamide remain either unperturbed or undergo slight positive shift. This opposite trend in the shift of NH and CO stretching modes indicates clearly that the carbonyl oxygen of isonicotinamide is not involved in coordination in these complexes. In addition, the increase of the NH stretching

Table 2. The infrared wavenumbers (cm^{-1}) of isonicotinamide molecule in the $M(iso)_2Ni(CN)_4$ (M = Cd, Zn, Ni, or Cu; iso = isonicotinamide) and $Cd(iso)_2X_2$ (X = Cl, Br, or I) complexes.

Iso	Cd	Zn	Ni	Cu	$Cd(iso)_2Cl_2$	$Cd(iso)_2Br_2$	$Cd(iso)_2I_2$	Assignment[a]
3370 vs	3465 s	3467 s	3451 s, sh	3444 s, sh	3407 vs	3425 vs	3422 vs	NH_2 asy str
	3409 vs	3405 s, sh						
3301 vw	3302 w	3313 w	3298 s	3301 s	3300 w	3295 w	3306 w	
3187 vs	3178 s	3165 s	3159 vs	3158 vs	3172 vs	3172 s	3180 s	NH_2 sym str
3063 m	3060 w	3066 w	3063 sh	3064 sh	3065 m	3062 m	3060 w	CH str (py)
1668 vs	1678 vs	1678 vs	1682 vs	1686 vs	1699 vs	1700 vs	1702 vs	C=O str (am)
1623 vs	1623 s	1628 m	1629 s	1629 s	1622 s	1621 m	1619 m	NH_2 def (am)
1595 s	1611 vs	1613 s	1617 s	1618 s	1611 vs	1607 vs	1604 m	Ring str (py)
1552 s	1557 vs	1558 s	1551 s	1552 s	1555 s	1555 m	1549 m	Ring str (py)
1496 w	1498 vw	1506 w	1504 vw	1507 vw				i.p. CH bend (py)
1458 vw	1456 sh	1456 sh	1457 vw	1456 vw	1459 vw	1458 vw	1456 vw	Ring str (py)
1410 vs	1417 vs	1421 vs	1418 vs	1425 vs	1417 vs	1415 vs	1417 s	CC str (py) + i.p.CH(py)
1391 vs	1386 vs	1400 vs	1400 vs	1399 vs, sh	1398 vs	1381 vs	1388 s	CN str (am)
1321 vw	1324 vw	1320 vw	1326 w	1326 w	1323 w	1324 w	1329 w	CC str (py)
1294 vw	1307 vw	1304 vw	1309 vw	1309 vw	1309 vw			i.p. CH (py)
1226 sp	1230 m	1229 m	1233 m	1233 m	1230 m	1234 m	1222 m	CH bend
1218 m	1217 sp		1220 sp	1220 sp	1216 m	1215 m	1216 m	CC str (py)
1148 m	1151 m	1155 m	1158 m	1153 m	1151 m	1147 m	1147 w	NH_2 rock (am)
1122 m	1120 w	1125 vw	1133 m	1133 m	1122 m	1118 m	1117 w	$C-CONH_2$ (am)
1084 w	1100 w	1105 w	1106 m	1106 m	1105 vw	1101 w	1098 w	CH bend (py)
1063 m	1065 s	1066 m	1063 m	1062 m	1065 m	1063 m	1063 m	Ring CCC bend
1001 vw								

(*continued*)

Table 2. Continued.

Iso	Cd	Zn	Ni	Cu	$Cd(iso)_2Cl_2$	$Cd(iso)_2Br_2$	$Cd(iso)_2I_2$	Assignment[a]
993 m	1016 s	1024 m	1030 m	1030 m	1016 s	1014 s	1011 m	Ring breat (py)
878 vw	878 vw	878 w	878 vw	878 vw	885 vw	890 vw	874 vw	o.p. CH (py)
853 s	850 s	852 m	856 s	856 s	850 vs	845 s	847 m	Breat (py)
797 s	809 w	816 m	808 w	807 w				o.p. CH (py)
777 m	784 vw		785 w	793 w	793 vw	790 vw	782 vw	CC ring breat (py)
757 m	765 m	759 m	761 m	761 m	765 m	760 s	765 m	o.p. ring def
707 w			704 sh	703 vw	717 vw	724 w	721 w	o.p. ring def (py)
671 s	693 vw	693 w	668 m	669 m	684 vw	680 vw	683 vw	Ring CCC bend
658 s	665 vw	667 w	657 m	657 m	665 vw	669 vw	667 w	NH_2 wagg (am)
627 vs	639 vs	645 s	642 s	642 s	638 vs	637 vs	631 vs	i.p. ring def
594 sh								
541 m	550 m	535 m	540 gm	539 m	555 m	548 m	540 m	Pl. ring def
					518 s	504 s		
486 sh			485 w	485 w				Ring torsion
443 vw	446 vw							
412 s	405 m	406 m	419 m	419 m	405 s	408 m	403 m	Nonpl ring def
Total shift	149	204	207	215	176	128	95	

Note: Py: pyridine; am: amide; asy: asymmetric; sym: symmetric; rock: rocking; str: stretching; i.p.: in plane; breath: breathing; o.p.: out of plane; p1: planar; def: deformation; vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder, sp: split, wagg: wagging.

[a] Taken from Ref.[2].

frequency in the complexes, with respect to the free iso, may be the result of restricted intermolecular hydrogen bonding interactions when the iso is involved in complex formation.

Pyridine ring vibrations of free isonicotinamide at 1595, 993, and 627 cm^{-1} shift significantly to higher frequencies in the spectra of these complexes. Also, it is known that the NH_2 group vibrational modes of aniline and aniline derivatives are much affected by complex formation.[11,12] For example, the NH_2 stretching bands move to lower wavenumbers on coordination. The significant shift of the NH_2 stretching bands to the lower frequencies, upon complex formation, has been explained as a weakening of the N–H bonds resulting from the electron drainage from the nitrogen atom because of its coordination to the metal atom.[12] These frequency analyses (Table 2) indicate conclusively that coordination of isonicotinamide takes place via the pyridine ring-nitrogen to the metal ions studied.

Although most metal halide pyridine complexes have been characterized crystallographically, there is a distinct lack of structural data for the isonicotinamide halide complexes studied here. However, since isostructural complexes are known to exhibit similar band patterns in their vibrational spectra,[13,14] in the absence of structural data on a given complex, it has been classified depending on its spectroscopic features.

The $Cd(iso)_2X_2$ ($X = Cl$, Br, or I) complexes are known to have a polymeric octahedral configuration.[1] The IR spectra of di-isonicotinamide complexes are given in Table 2. As can be seen from the Table 2, several vibrational modes of iso have upward shifts in frequency when compared with the free iso values. The total shift values of tetracyanonickelate and halide complexes of iso are given at the bottom of Table 2. We note that the general increase in frequency of the iso modes with the different metals in tetracyanonickelate complexes is in the order: $Cd < Zn < Ni < Cu$, which is in agreement with the increasing order of the second ionization potential of the metals. Analogous shifts on coordination were observed in the vibrational spectra of pyridine tetracyanonickelate and halide complexes[13–15] and explained as the coupling of the internal modes of the aromatic molecule with the M–N (iso) vibrations. It is noted that for the isomorphous halide complexes the shift values depend on the halogen for a given cadmium metal it decreases in the order $Cl > Br > I$.

3.2 The $Ni(CN)_4$ Group Vibrations of the $M(iso)_2Ni(CN)_4$ Complexes

The wavenumbers of the $Ni(CN)_4$ group vibrations of the compounds studied are tabulated in the Table 3, together with the vibrational

Table 3. The infrared wavenumbers (cm^{-1}) of the $Ni(CN)_4$ group vibrations of the $M(iso)_2Ni(CN)_4$ (M = Cd, Zn, Ni, or Cu; iso = isonicotinamide) complexes.

Assignment	$Na_2Ni(CN)_4$[a]	Cd–Ni-iso	Zn–Ni-iso	Ni–Ni-iso	Cu–Ni-iso
E_u ν(CN)	2132	2155 vs	2156 vs	2164 s	2165 s
		2142 vs	2143 vs	2138 vs	2139 vs
$\nu(^{13}CN)$	2128	2115 sh	2115 sh	2101 sh	2102 sh
E_u δ(NiCN)	433	428 s	429 s	447 s	447 s
		416 s	417 s	441 s	442 s

[a]Taken from Ref.[16].

wavenumbers of $Na_2Ni(CN)_4$. In the IR spectrum of $Na_2Ni(CN)_4$, the CN stretching vibrational mode was observed at 2132 cm^{-1}.[16] For the corresponding modes of $M(iso)_2Ni(CN)_4$ complexes an upward shift is observed. The IR spectrum of the $Cd(iso)_2Ni(CN)_4$ complex is given in Fig. 2. The ν(CN) and δ(NiCN) vibrational frequencies are also found to be similar to

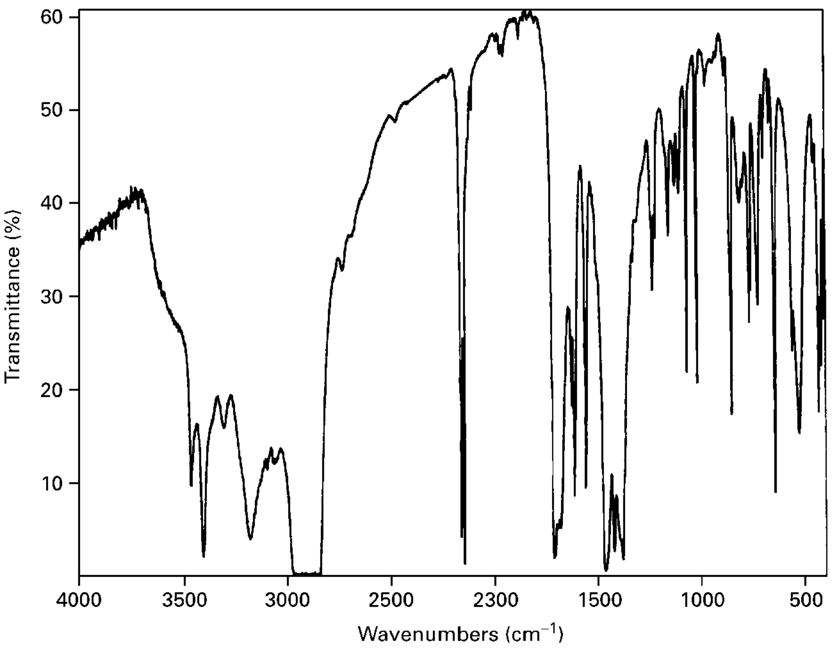

Figure 2. The infrared spectrum of $Cd(iso)_2Ni(CN)_4$ complex (in Nujol).

the Hofmann-type clathrates[5] and aniline complexes[12] indicating that the $|M-Ni(CN)_4|_\infty$ polymeric layers have been preserved.

If the cyanide groups around the nickel atom have a local D_{4h} environment, one ν(CN) (E_u) band only is expected in the IR spectrum. However, two strong bands, rather than one are observed in the ν(CN) (E_u) and also the δ(NiCN) (E_u) regions of the IR spectra of the $M(iso)_2Ni(CN)_4$ [M = Cd, Zn, Ni, or Cu] complexes. The splitting points directly to a change of symmetry and removal of the degeneracy. Similar splitting was observed in the ν(CN) (E_u) and also δ(NiCN) regions of the IR spectrum of the Cd $(aniline)_2Ni(CN)_4$ complex.[12] The ν(CN) frequencies are found to be slightly dependent on the metal (M). This is probably due to the changes of the strength of the M–NC bonds, since it is known that there is a mechanical coupling between the M–N and C≡N stretching modes.[15]

CONCLUSION

This IR spectroscopic study of four new Hofmann-type complexes has shown that they have structures consisting of polymeric layers of $|M-Ni(CN)_4|_\infty$ with the iso molecules bound directly to metal (M). It was found that frequency shift values depend on the metal in the order: Cd < Zn < Ni < Cu, and for cadmium halide complexes the shift values also depend on the halogen, and decreases in the order Cl > Br > I.

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